UNITED
NATIONS

ST

Secretariat

Distr.
GENERAL

ST/SG/AC.10/C.3/1997/64
26 September 1997

Original: ENGLISH

COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS

**Sub-Committee of Experts on the
Transport of Dangerous Goods
(Fourteenth session,
Geneva, 8-18 December 1997,
agenda item 4 (b))**

GLOBAL HARMONISATION OF SYSTEMS OF CLASSIFICATION AND LABELLING OF CHEMICALS

Physical hazards

Joint ILO/UN Working Group on Harmonised Classification Criteria for Flammability and Reactivity

Testing Conditions for Solids

Transmitted by the Expert from the United Kingdom

Background

1. Discussions on the global harmonisation of classification and labelling systems (GHS) have highlighted that for some end points the physical condition of a substance may affect the classification. This is particularly relevant for solid materials where differences in particle size are likely to influence the test results. Some discussion of the subject has taken place, particularly in relation to solid oxidisers, but there is the need to address the issue for all end points as a matter of principle. In paper ST/SG/AC.10/C.3/1997/28 the Chairman of the working group raised this issue under "Testing Conditions for Solids", and proposed some useful ideas for discussion. This paper is intended to build on that document and proposes how the problem may be resolved in principle.

2. A fundamental concept of the GHS is that classification should be based on the intrinsic properties of substances. For solids, however, this concept is not helpful. Classification is determined relative to a standard which may be either a defined reference material or an absolute value. It is well recognised that for a specific solid chemical substance, the results obtained from a test may vary with the physical form of the material. Examples of factors known to affect test behaviour are particle size, crystal form and density. The resulting assignment into a hazard category can range from low to high danger, or the classification may change completely. A change in the physical form of a substance may leave the material either unclassified or assigned to a different hazard category.

3. Therefore, it may not be possible to have a single classification for specific solid substances. A solid may have a number of classifications depending upon certain critical parameters, and these will vary from substance to substance.

Current position

4. In the context of the intrinsic properties of a chemical substance, the idea of multiple classifications may be considered contentious, but it is already used in practice. For example, within the EU supply system (67/548/EEC) a number of metals are only classified when in powder form (e.g. alumimium powder (pyrophoric) EEC No 013-001-00-6 and aluminium powder (stabilised) EEC No 013-002-00-1 are both highly flammable). It is also reflected in general terms within the UN Recommendations, where special provision 185 or 223 can be applied; application of these special provisions often reflects the variability of behaviour in classification tests with changes in physical form. Specific multiple classifications in the transport list in Chapter 2 of the UN Recommendations include:

Ammonium perchlorate: classified as 1.1D (UN 0402) or 5.1 (UN 1442) with reference to its particle size, but based on test data.

Titanium (metal): has entries for dry powder UN 2546 (Div. 4.2) and sponge powders or sponge granules UN 2878 (Div. 4.1).

Titanium powder wetted: there are two particle size limits specified under the single Chapter 2 entry of UN 1352, these depend upon whether the powder is produced mechanically (53 mm) or chemically (840 mm); (see also Hafnium powder wetted UN 1326).

5. Under most circumstances testing in the form presented is appropriate e.g. classification of a metal powder should be based on the properties exhibited by the powder, not the properties of a block or granules and vice versa. A metal in the form of lumps or a coarse powder may not burn, finer powders may burn sufficiently rapidly to be classified as flammable solids, and very fine powders may be pyrophoric. However, it is not possible to predict whether or not a particular material will exhibit this range of behaviour and if so where the thresholds will occur. An educated guess can be made and may often suffice, but in practice thresholds will not be sharp. If the form of the material is changed, it may be possible to predict if the new form will behave in a similar way or if retesting is necessary, but frequently this will be limited to either minor or gross changes. Actual thresholds for changes in behaviour will need to be determined by testing, when the need arises.

6 The situation is even more complicated when classification is based on composite data (e.g. detonation, deflagration and heating under confinement). Examples where variability is observed or expected include ammonium nitrate, where density may be critical, and materials where the significant test for classification is the deflagration behaviour, when the rate of deflagration can be markedly affected by particle size.

7. A classification should therefore only apply to a substance in an appropriately defined form. This would allow materials to be classified on the basis of tests performed on "the form presented", and would ensure that classification represented, as far as is practicable, the behaviour of the material in question. It is appropriate therefore that, if testing in the form presented is adopted, the form is appropriately specified.

Special consideration of oxidising solids

8 UN test O.1: Test for oxidizing solids should be considered an exception to the principle of testing in the form presented. This is based on two factors:

(1) the definition of a solid oxidiser; and
(2) a small scale laboratory test for classification is intended to predict large scale behaviour.

9 The definition of an oxidiser refers to a substance which may assist a fire "generally by yielding oxygen" (UN Recommendations para. 2.5.1 (a)). In para 34.4.1.2.1 of the Manual of Tests and Criteria the particle size of the reference material is specified, this is so that an intimate mixture with cellulose can be obtained, and the burning rate of the mixture can be examined. The reference material is only ground if fine material (<500 mm) constitutes more than 10% of the mass of the sample or the material is friable (Test Manual 34.4.1.2.6). In practice, if a substance under the influence of heat can decompose to produce oxygen, relatively coarse material will do so in a real fire scenario. In a small scale test such as is Test O.1, even a solid the size of fertiliser prills is so coarse, relative of the size of the pile, that obtaining a suitable mixture and subjecting it to a meaningful heat challenge is almost impossible. This is certainly case for prilled ammonium nitrate fertilisers which are currently assigned UN Division 5.1, and which give negative results in small scale pile tests. A classification based on the behaviour of coarse material in a small scale test is not therefore representative of "real-life" behaviour. In the case of the oxidiser test for solids it is more appropriate to compare like with like, i.e. to test the sample in the same particle size range as that of the standard.

10. It is not always possible to grind a material prior to test, for example a waxy solid would require specialist (cryogenic) milling equipment, and under these circumstances it is reasonable to dispense with the requirement to mill. However as by far the majority of solid oxidisers are crystalline inorganic substances, this dispensation will not have a significant impact.

Proposals

11. For classification tests on solid substances (except for solid oxidisers), the tests should be performed on the substance as presented. If, for the purposes of supply or transport, the same chemical is to be presented in a different physical form which is considered likely to materially alter its performance in a classification test, the substance in the new form must be tested.

12. The technical name shall include information on the physical form of the substance, if this affects the classification.

13. If such a scheme is accepted within the GHS, then clear guidance would need to be prepared to ensure that testing was not required or demanded for every possible material form of a substance. If it is reasonably foreseeable that the material form of a substance will change significantly through its lifecycle then the potential hazards must be addressed. If the hazard is potentially increased so as to change the classification then this should be dealt with by way of calculation, inference, or in exceptional circumstances by further testing.

14. For UN test O.1 Test for Solid Oxidisers, where it is practical to grind the test substance, the test shall be performed on the substance in the same particle size range as the potassium bromate reference.